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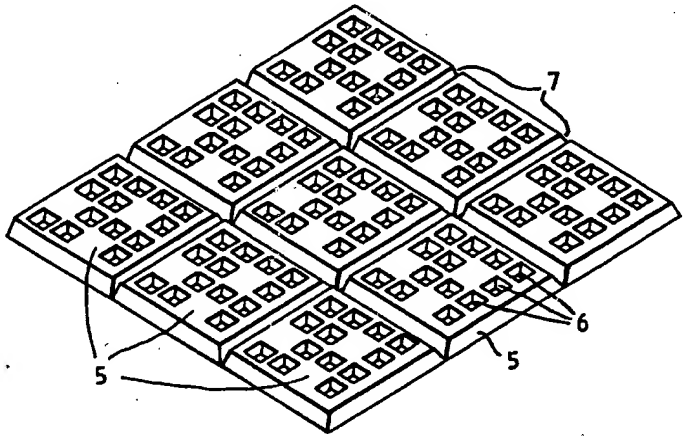

(57) Abstract

This invention relates to an improved method of fabricating silicon microparticles (5, 10, 12, 18, 20, 23, 26), each microparticle (5, 10, 12, 18, 20, 23, 26) carrying a machine readable binary code in the form of holes (2, 3, 6, 13, 15, 17, 24, 27), pits, or other optically identifiable marks. The microparticles (5, 10, 12, 18, 20, 23, 26) may be manufactured in sizes from a few tens of micrometres up to millimetres in linear dimension and simultaneously manufactured in numbers of up to the order of one million from a single silicon wafer (1, 4, 16), depending upon particle size. The process of manufacture is based upon direct etching of silicon wafers (1, 4, 16). Microparticles (5, 10, 12, 18, 20, 23, 26) of a few tens of micrometres length and breadth, which are essentially invisible to the naked eye, may be manufactured by this process for use in security and anti–counterfeiting applications of valuable goods, paper currency, etc. Larger particles (5, 10, 12, 18, 20, 23, 26) of up to several hundred micrometres in length and breadth which additionally carry a quantity of appropriate combinatorial chemistry support polymer resin (11, 14, 19, 21, 25, 29) in the form of a layer or a bead may be made for use in combinatorial compound library (CCL) synthesis.

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An Improved Method of Fabricating Coded Particles

Field of the Invention

The present invention relates to an improved method of fabricating coded particles. It is particularly applicable, but in no way restricted, to the fabrication of coded security particles and coded combinatorial chemistry support particles.

Background to the Invention

A method has been described in GB 2 289 150 B by which small microparticles may be manufactured by the process of silicon micromachining, each microparticle carrying an identifying code in the form of holes, pits, or similar marks constituting a machine readable binary number. The microparticles may be fabricated from typically silicon or silicon dioxide, and have dimensions in the approximate range 0.1μm to 5μm thickness and 0.5μm to 50μm width and length, rendering them essentially invisible to the naked eye. Suspensions of the coded microparticles (either gaseous, such as in smoke, or liquid such as in paint, clear varnish or ink) would find application in security systems as they may be used to uniquely label items such as consumer durables (cars, motorcycles, electrical appliances) or other valuables (jewellery). Such labelling could be undertaken either during manufacture or at any time subsequently. Similarly, the microparticles could be employed in security printing (particles impregnated in paper or in suspension in printing inks) for items including banknotes or negotiable securities or in other documentation (driving licences, passports, identity cards) where security and uniqueness is a consideration. Identification of the particle codes could be achieved using a hand-held or desktop optical reader similar to bar code readers used in supermarkets. The technology used

of deposition and etching to those used to make microelectronic integrated circuits. The fundamentals of the fabrication of the microparticles is described by Kaye et. al. in the Journal of Aerosol Science Vol. 23 [1992, Supplement 1, 201-204] and involves typically:- the design of the required particle geometry (or geometries) using computer aided design (CAD) tools; the manufacture of appropriate photolithographic masks which delineate both the microparticle outlines and the required coding marks within the microparticle outlines; the growth by vapour deposition onto a polished silicon wafer (typically 3, 4 or 8 inches in diameter) of a thin layer of material such as aluminium, this to become a sacrificial bonding layer (see below); the growth by vapour deposition or similar process, onto this sacrificial layer of a further layer of, for example, silicon or silicon dioxide from which the particles will be ultimately be formed; the coating of this layer with a photosensitive polymer resist (photo-resist) which, upon ultraviolet exposure through the photolithographic mask, defines the microparticle shapes and the locations of coding marks; the removal of exposed photo-resist thus revealing areas of the underlying layer of silicon or silicon dioxide; and finally the creation of the microparticles with their associated code marks within this layer by etching away the revealed areas of the layer between the microparticle outlines and within the areas designated as code marks. The particles may then be freed from the wafer substrate by dissolution of a sacrificial layer which underlies the particles. The sacrificial layer is typically made of aluminium if the particles are of silicon dioxide, and of silicon dioxide if the particles are of silicon.

In the case of the microparticles for combinatorial chemistry, an additional processing stage is required before the microparticles are freed from the wafer substrate. In this additional stage, each coded microparticle receives its quantity of polymer support

support polymer per particle, a thickness of less than 10μm leads to a high surface area to thickness ratio and consequently a mechanically less robust particle. In many areas of use, the particles will have to endure mechanical stress, and particles which exhibit a thin wafer-like form are far more likely to suffer breakage than those of a more isometric geometry.

Secondly, layers grown in the way described above are generally of amorphous form, as in the case of silicon dioxide, or are polycrystalline (being formed from vast numbers of randomly aligned crystallites) as in the case of silicon. In either case, the resultant particles may be comparatively brittle and not as mechanically strong as, for example, single crystal silicon, the material of the supporting wafer upon which the particles are formed.

Thirdly, the release of the etched microparticles from the host silicon wafer (as described in Kaye et al, ibid) requires the dissolution of the thin sacrificial layer between the two. In the case of silicon dioxide particles, this layer may be of aluminium and its solvent concentrated hydrochloric acid. For small surface-area microparticles the removal of this sacrificial layer is not problematic. However, for larger area particles, as would be required in the combinatorial chemistry application, the dissolution of the sacrificial layer can become severely impeded as it progresses into the crevice between the microparticle and the host wafer by the formation and entrapment of bubbles of hydrogen. Unable to escape and very difficult to remove by external agitation, these bubbles effectively insulate the remaining aluminium from attack by the acid, leaving a proportion of the microparticles to all intents and purposes permanently attached to the host wafer and therefore of no practical use.

Summary of the Invention

According to a first aspect of the present invention there is provided a method of fabricating coded particles comprising the steps of:-

(a) coating a face of a wafer of silicon or a similar crystalline material or inert metal or metal alloy with a photo-resist polymer;

(b) exposing the coated face of the wafer to ultra-violet radiation through an appropriate photolithographic mask, said mask defining the particle size and/or the position of code sites on the particle;

(c) dissolving or otherwise removing either the UV exposed or the UV unexposed areas of photo-resist;

(d) etching the exposed areas of the wafer, from which the photoresist has been removed, using an appropriate etching agent; and

(e) liberating the particles.

This process avoids the disadvantages inherent in conventional micromachining techniques for fabricating coded particles

In a preferred embodiment the wafer is first attached to a stable substrate such as a glass plate, using a thin adhesive layer such as, for example, a layer of wax. The final step in the process is removing the particles from the substrate suitably by dissolving the adhesive or the substrate. This additional feature is particularly applicable to the manufacture of larger particles for use in combinatorial chemistry.

Preferably the step of etching the wafer comprises plasma etching the exposed areas of the wafer through to the opposing face of the wafer.

In a still further aspect of the invention there is provided a combinatorial library prepared using the above support particles, regardless of the chemical reactions or sequences used to prepare said library.

The present invention also provides a method of reading codes comprising the steps of:

(a) placing the particles to be read in a substantially flat, substantially horizontal vessel with a transparent bottom, the area of the bottom being at least double the total area of the particles to be measured;

(b) agitating the vessel to form a monolayer of particles on the bottom; and

(c) scanning the vessel with an imaging system whilst illuminating the particles.

Brief Description of the Drawings

The present invention will be further described, by way of example only, by reference to the accompanying drawings in which:-

Figures 1 & 2 illustrate perspective and cross-sectional views of typical pyramidal holes etched through a silicon wafer by potassium hydroxide etching agent;

Figure 3 illustrates an array of particles etched with holes as shown in Figures 1 and 2;

Figure 4 illustrates a cross-section of a series of particles set in a layer of wax on a glass plate;

Figure 5 illustrates a coded particle with a layer of polymer adhered to part of its surface;

Figure 6 illustrates a cross-section of a particle with polymer set within a hole in the particle;

down to 5μm. The wafer diameters may be typically 2 inches or 3 inches. The crystal orientation of the wafers is usually <100>. One company who manufacture these wafers is Virginia Semiconductor Inc., of 1501 Powhatan Street, Fredericksberg, VA 22401, U.S.A. One property of single crystal wafers of this type is that certain wet chemical etchants, such as potassium hydroxide (KOH) and ethylene-diamine-pyrocatechol – water (EDP), will attack the silicon anisotropically, with the effect that the silicon is removed only to a point where a <111> crystal plane is encountered. This means that if, for example, a square area of the surface of the silicon is exposed, the KOH will etch down into the silicon to form a four sided pyramidal pit whose sides represent the four <111> crystal planes. The atomic structure of silicon dictates that these planes will be at 54° to the <100> plane (the surface of the wafer). If the wafer is thin in comparison to the diameter of the exposed surface, the etched pit may extend completely through the opposite surface of the wafer, leading to the formation of a hole through the wafer. Figure 1 illustrates a section of thinned silicon wafer 1 containing such a pyramidal hole 2 . This feature can be put to use in the fabrication of coded microparticles. The following description is a preferred but not the only method of processing a thinned wafer to produce such particles.

The preferred thickness of the original silicon wafer is in part determined by the size requirements of the desired coded particles and the nature of the code marks themselves. It is most beneficial when dealing with opaque materials such as silicon for the code marks to be in the form of holes through the complete particle thickness rather than simply surface features, this being because holes allow clear identification of the code sites by transmission illumination of the particle. If, therefore, a particle is desired to have surface dimensions of 100μm by 100μm, and if it is desired that each

photo-resist layer on the lower surface. The code site holes will have been etched too. Figure 3 illustrates the appearance of some of the particles 5 with the code site holes 6 etched in the particles and the inter-particle silicon 7 removed to produce separated particles. Given that the etched area between the particles will be of width approximately 12μm at the upper surface (ensuring a 5μm particle separation at the lower surface), the number of 50μm square particles which could be formed on a 3 inch wafer would be approximately 500,000 with each particle carrying a 16-bit binary code. The final stage is to free the particles from the photo-resist layer by immersion in a further solvent routinely used for removing unexposed photo-resist. The freed particles will sink to the bottom of the vessel containing the solvent, and may be pipetted into a separate container for further washing and ultimate preparation as a dry powder or as a liquid suspension in, for example, a clear lacquer.

The above method offers significant advantages over the current art. Firstly, the particles may be made by this method in almost any size from a few tens of micrometres width and breadth to millimetre-sized width and breadth. Larger particles should be proportionally of greater thickness so as to retain mechanical strength, and this will have a subsequent effect on the spacing between code mark sites because of the pyramidal geometry of etched-through holes. Thicker wafers will require proportionally greater separation between the code mark sites because the dimensions of the pyramidal holes at the upper surface will be scale with particle thickness. Secondly, the particles are made from single crystal silicon, making them stronger and more mechanically robust than particles produced by the layer growth method. Thirdly, because there is no sacrificial layer to be removed so as to free the particles (as is the case in grown-layer particle fabrication), there are no attendant

spherical polymer bead. These methods are described below. All the methods are based upon the aforementioned particle fabrication process using thinned silicon wafers as described earlier for the security coded particles, with an important additional feature: when the particles, and associated code marks, have been etched as described above and the particles are still attached to the photo-resist layer covering their lower surfaces, the polymer resin must be attached in some way to the particles. The photo-resist layer is too weak to hold the particles firmly whilst this operation is carried out, and a more rigid temporary support for the particles is required. One method of achieving this support is to attach the original naked thinned silicon wafer to a strong flat glass plate using a very thin layer of wax or similar substance. Paraffin wax is useable, but any wax-like material which is impervious to wet chemicals (such as KOH), which is solid and firm at room temperature, which has a melting point above the temperature required for polymerisation of styrene (see below), and which has reasonable adhesion to both the silicon wafer and the glass plate, may suffice. The upper surface only of the wafer is then coated with photo-resist and the particle fabrication process proceeds as before. Once the particles (and code marks) have been etched using KOH, the particles will remain in their relative positions held by the wax layer. Figure 4 illustrates in cross-section this configuration of glass plate 8 with a coating of wax 9 supporting the etched particles 10. As mentioned, the step of attaching the polymer resin to each particle may take various forms, examples of which are described below:

In the simplest method, a thin (typically 25μm) mask of a suitable material such as stainless steel, which has holes etched in it in positions defined such that, when the mask is placed over the particle array held on the wax, the holes align with areas on

mask but this time the monomer fills the new hole(s) in the particle. The remainder of the processing is as before, and the final particle would take the form illustrated in Figure 6, with the polymer 14 retained within the large hole or holes 15 in the silicon wafer 16, leaving the code site holes 17 unobscured and viewable using a suitable microscope imaging system or similar. The advantage of this method of attaching the polymer to the silicon particle is that the exposed surface area of the polymer is maximised, thus enhancing the polymer's performance in acting as a substrate for compound growth in subsequent combinatorial compound library synthesis.

By way of example, a further embodiment of the method of attaching a polymer resin to a coded silicon particle is described now. The thinned silicon wafer is attached as before to a rigid glass plate using an appropriate wax or similar bonding agent. The particles and associated code holes are etched, but an additional large hole is etched at the same time within each silicon particle. This large hole will be of essentially square form and, in accordance with the nature of KOH anisotropically etched holes, will have side walls at 54° to the horizontal particle surface. The size of the hole is designed such that a conventional polymer resin bead (as currently used in combinatorial compound library synthesis) may be selected with a diameter which is less than the aperture in the upper surface of the silicon particle but greater than the aperture in the lower surface. Whilst the silicon particles are still held in place on the wax bonding layer, the whole of the area covered by the silicon particles on the glass plate is immersed in dry polymer beads. Single beads will become lodged in the large etched holes, like marbles in a bagatelle board, such that when the glass plate supporting the silicon particles is tilted sufficiently, loose beads will roll off, leaving

However, one disadvantage of this initial approach is that, because the holes are pyramidal, their size (in order to penetrate through the particle) is governed by the wafer thickness from which the particle is formed, with thicker wafers requiring larger and more widely spaced code-holes. For thicker wafers therefore, this can limit the size of the code number which the particle can support.

In a further embodiment of the invention most suited to combinatorial chemistry applications, double-sided polished silicon wafer is suitably first anodic-bonded to a substrate material such as glass or by other means to other rigid material such as an organic solid. In the preferred embodiment a Pyrex glass wafer is used.

However, any suitable substrate may be used which has sufficient mechanical strength and chemical stability to withstand the rest of the process. This includes certain rigid polymers and wax blocks, such materials being selected by the materials specialist.

The upper surface of the silicon wafer is then coated with an appropriate photoresist material which is subsequently exposed to ultraviolet radiation through a photolithographic mask which defines the size and shape of the particles and their respective code marks. The particle size thus defined will be selected in accord with the wafer thickness, such that the length and width dimensions of the particle are preferably several times the particle thickness so as to ensure a high probability that a free particle will lie horizontally, thus facilitating code reading. For a 300 micrometre thick wafer therefore, particles of the order of 700 micrometres square would be appropriate. Thinner wafers would allow commensurately smaller cross-

for the subsequent adhesion of polymer resin, as described below.

The support compound for combinatorial chemistry synthesis is then affixed to to each particle, mechanically or chemically, to provide the compound growth platform. In a preferred embodiment, the afore-described method of 'silk-screening' the polymer onto each particle is used.

The polymer mix, prior to curing and consequent cross-linking, is applied though the "silk-screening" mask using a screeding, painting, or rolling process. The silicon dioxide surface may also be advantageously pre-treated with a silane compound designed to provide a 'coupling' functionality between the silicon dioxide and the polymer, hence promoting good adhesion. Also, the area of the particle surface to which polymer is to be applied may itself be etched by appropriate masking and plasma etching to leave a well or wells into which the polymer is forced, again promoting good adhesion between the particle and the polymer.

The use of a silk-screen mask in this way allows accurate simultaneous deposition of polymer to each particle on the wafer, possibly many thousands of particles in total. As indicated in Figure 11, each particle 23 would thus exhibit a code in the form of holes 24, and an area or several separate areas of polymer 25. The exact positions of code holes and polymer would be such as to ensure unobscured viewing of the code holes 24. Once the polymer 25 has been deposited in this way, the temperature of the whole wafer assembly may be raised to an appropriate level to ensure cross-linking of the polymer takes place, whereupon the bond between the polymer and the particle becomes permanent. Finally the resulting polymer-

the silicon wafer to produce the coded particles proceeds as before, but with the addition that a locating hole is etched in each particle into which a polymer resin bead will subsequently be positioned. As illustrated in figure 12, the particle 26 would exhibit code holes 27 plus a bead entrapment hole 28 which is of a size and form designed to rigidly hold the bead 29 in position whilst allowing the bead 29 to act as a suitable substrate for compound synthesis.

A preferred method by which the beads are positioned in the entrapment holes is as follows. The beads are known to swell and contract when in contact with the various organic solvents used in combinatorial chemistry. It is essential that the bead and host coded silicon particle remain in contact throughout the combinatorial process. The size of the entrapment hole is therefore chosen to be fractionally less than the smallest size which the bead is likely to assume during processing. This would normally occur when the bead is immersed in diethyl ether or similar reagent. The polymer beads may be linked to the silicon particles in the following way. When the silicon particles are etched but still attached to the glass substrate, the suitable population of resin beads is prepared by immersion in diethyl ether, causing them to contract to minimum dimensions. The collection of beads is then poured over the wafer surface and a roller or similar device used to compress the beads against the silicon particles. In areas where a bead becomes positioned over an entrapment hole, the bead will be forced into the hole. Repeated cycles of this process will ensure that the vast majority of the particles entrap a bead. Loose particles may then be flushed away and the wafer immersed in hydrofluoric acid as before to release the particles from the glass substrate. Each silicon particle will then contain a polymer resin bead exposed on upper and lower surfaces, allowing expansion of

flat, so that particle overlapping is minimised. The vessel is then placed onto a suitable mechanically driven stage which allows movement of the vessel in either an 'x – y' motion 'or x + rotation' motion. The vessel is then viewed from above by the stationary imaging system which is capable of acquiring still images of the particles. By moving the stage in an 'x – y' raster scan beneath the imaging system, it can be ensured that all the particles contained within the vessel are at some time brought within the field of view of the imaging system, and their code information recorded. Alternatively, an 'x + rotation' motion stage will allow the surface of the vessel to be scanned in either a spiral scan or a series of concentric circular scans. Again, at some time all particles will be brought within the field of view of the imaging system. Illumination of the particles can be from below, in which case the code holes appear as bright spots against a dark background, or from above, in which case (because of the surface reflectivity of the silicon) the code holes appear as dark spots against a light background. Both forms of illumination can be used sequentially to ensure optimal imaging of the particles and hence greatest accuracy in reading the codes. The process of reading the code information from the recorded images of particles is as described in GB 2306484 B. It would also be possible to configure the mechanically driven stage such that the vessel is vibrated rapidly. This may be useful to ensure at the start of the scanning process that any particles which rested on their side would topple to the more stable flat orientation required for code reading. In the normal course of events, however, the particles are considered to be static within the vessel such that the images of the particles can be used to not only determine the codes on individual particles but also, in conjunction with a knowledge of the stage motion, the position of each particle can be evaluated. Knowledge of the position of each particle at and after the final code reading

Libraries (CCL's) are porous silicates, for example controlled pore glass, polymeric resin materials for example polystyrene; poly(substituted-styrene), for example poly(halomethylstyrene), poly(halostyrene), poly(acetoxystyrene); polyacrylamides, for example poly(acryloylsarcosine methyl ester); other polyesters, polyacrylates and polymethacrylates; as well as derivatised versions of these resins, for example polystyrene which has been chloromethylated, or poly(acryloylsarcosine methyl ester) wherein the ester has been saponified and the resultant acid derivatised with another moiety of utility in CCL synthesis, as well as optionally cross-linked versions of these resins.

5. A method as claimed in claim 3 or claim 4, wherein in the step of etching the exposed areas of the wafer one or more areas are etched to provide a recess or cavity into which the combinatorial chemistry support polymer is subsequently entrapped.

6. A method as claimed in claim 1 or claim 2 wherein the step of etching the exposed surface of the wafer is carried out using plasma etching whereby the wafer is etched right through to the opposing face of the wafer.

7. A method as claimed in claim 1 or 2 wherein the wafer is a single crystal wafer and the step of etching the exposed surface of the wafer is carried out using potassium hydroxide or another suitable anisotropic wet chemical etchant to etch the wafer anisotropically.

8. A method as claimed in claim 3, 4 or 5, wherein prior to the step of applying the combinatorial chemistry support polymer there is a further step of depositing silicon dioxide onto the exposed surface of the particles to assist binding of the combinatorial chemistry support polymer.

9. A method as claimed in claim 8, wherein the silicon dioxide is treated with a silane compound to further improve binding of the combinatorial chemistry polymer.

10. A method as claimed in any preceding claim, wherein the code is a machine readable binary code.

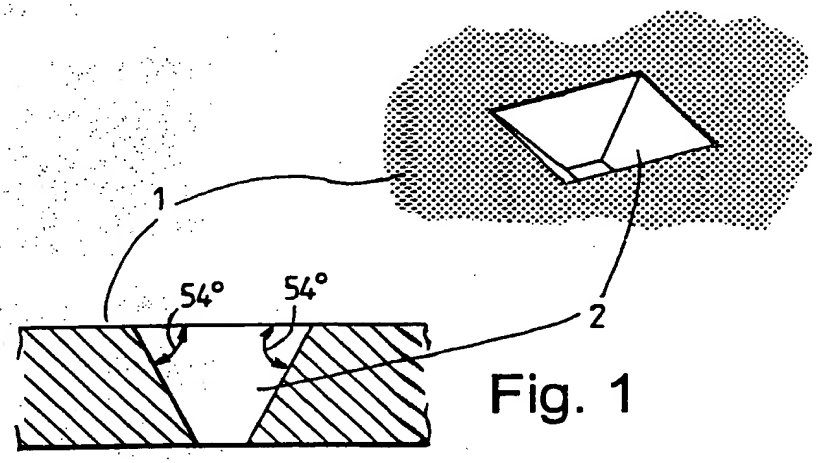

Fig. 1

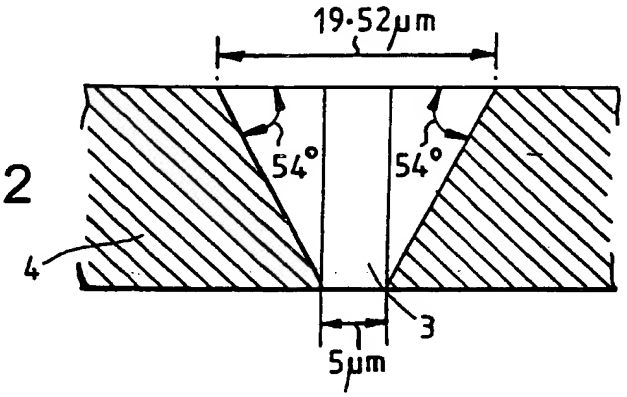

Fig. 2

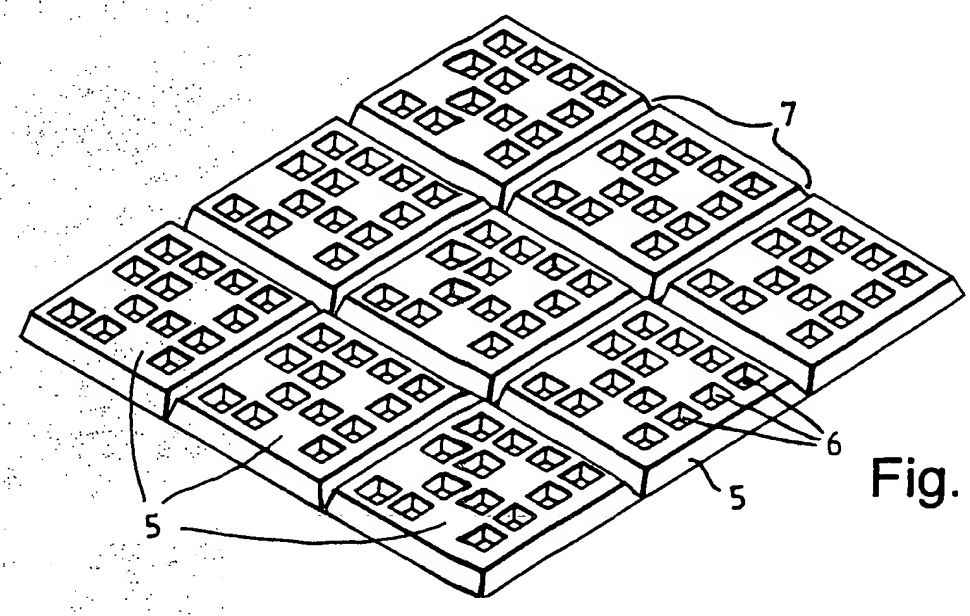

Fig. 3

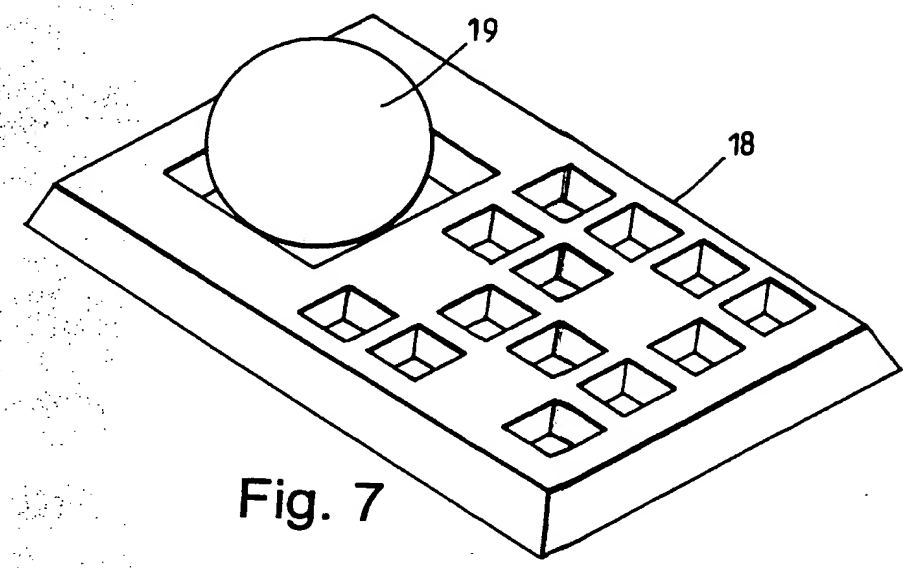

Fig. 7

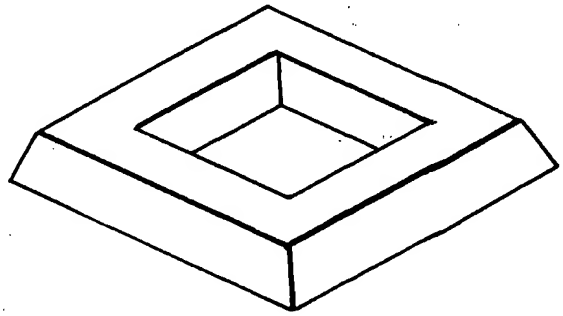

Fig. 8

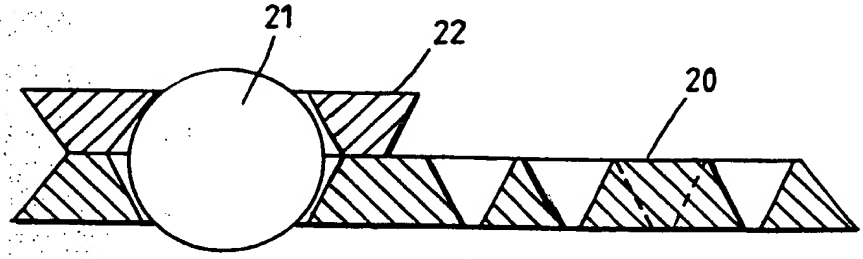

Fig. 9

INTERNATIONAL SEARCH REPORT

Inte 'onal Application No
PCT/GB 99/00457

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J19/00 B01J13/02 G03F7/00 G09F3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J G06K G09F G03F B81C B81B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2 306 484 A (UNIVERSITY OF HERTFORDHIRE) 7 May 1997 cited in the application see page 6, line 24 - page 8, line 11 see page 9, line 21 - line 26 see page 10, line 16 - page 18, line 12 see page 19, line 24 - page 21, line 14 see figures	1,3,5, 10-16
A		4,8,9

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
18 May 1999	04/06/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Stevnsborg, N

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INTERNATIONAL SEARCH REPORT

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PC1/GB 99/00457

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